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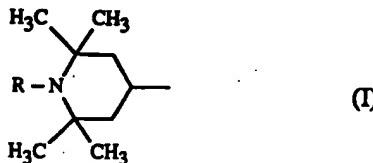
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(54) **Stabiliser compositions for polypropylene, comprising triazine compounds containing piperidine groups, and metal compounds.**

(57) The present invention relates to a stabiliser composition for polypropylene, comprising :
 A) one or more triazine compounds containing groups of the formula (I) in which R is hydrogen, $\text{C}_1\text{-}\text{C}_4$ alkyl, O^\bullet , OH, $\text{C}_1\text{-}\text{C}_8$ alkoxy, $\text{C}_5\text{-}\text{C}_8$ cycloalkoxy, $\text{C}_3\text{-}\text{C}_6$ alkenyl, $\text{C}_7\text{-}\text{C}_9$ phenylalkyl or $\text{C}_1\text{-}\text{C}_8$ acyl, and
 B) one or more oxides and hydroxides of Mg, Ca, Ba, Zn, Al and Sn, preferably Mg and Zn.



EP 0 468 923 A2

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The present invention relates to a novel method of stabilising polypropylene against photooxidative degradation by means of mixtures of derivatives of 2,2,6,6-tetramethylpiperidine and particular metal compounds.

It is known that polypropylene is susceptible to considerable changes in physical properties, such as a reduction in mechanical strength and a change in colour, if it is exposed to sunlight, due to photooxidative degradation caused by ultraviolet radiation.

To overcome this disadvantage, it is necessary to add suitable light stabilisers to the polymer, for example certain derivatives of benzophenone and benzotriazole, nickel complexes, esters of substituted benzoic acids, aromatic oxamides and sterically hindered amines.

However, the results obtained are greatly affected by the type of application of the polymer, such as mouldings, films, tapes or fibres.

The stabilization of polypropylene in fibre form involves particular difficulties; for this application, it is necessary to use products of relatively high molecular weight, which are resistant to evaporation and extraction.

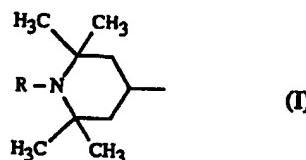
Good results have been obtained with some triazine derivatives of 2,2,6,6-tetramethylpiperidine, such as those reported in US Patents 4,086,204, 4,108,829, 4,288,593, 4,315,859, 4,321,374, 4,331,588, 4,335,242, 4,376,836, 4,433,145, 4,459,395, 4,477,615, 4,533,688, 4,547,548 and 4,740,544, European Patents 94,048, 117,229 and 176,106 and Japanese Patent 61/176,662.

The results obtained so far have, however, not been completely satisfactory, so that a further improvement was desirable.

It has now been found, surprisingly, that the use of mixtures of one or more triazine derivatives of 2,2,6,6-tetramethylpiperidine and one or more particular metal compounds in the light stabilization of polypropylene fibres gives significantly higher values than the use of the piperidine compounds alone.

In particular, the present invention relates to a novel method of stabilizing polypropylene, which comprises using synergistic mixtures consisting of:

A) one or more triazine compounds containing groups of the formula (I)



In which R is hydrogen, C₁-C₄alkyl, O-, OH, C₁-C₈alkoxy, C₅-C₈cycloalkoxy, C₃-C₈alkenyl, C₇-C₈phenylalkyl or C₁-C₈acyl, preferably hydrogen or methyl, and

B) one or more oxides and hydroxides of Mg, Ca, Ba, Zn, Al and Sn, preferably Mg and Zn.

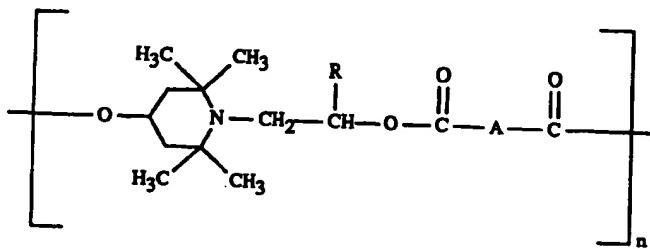
The use of some derivatives of 2,2,6,6-tetramethylpiperidine in a mixture with oxides or hydroxides of Mg or Zn for the stabilization of polyurethanes has been described in Japanese Patent 82/34,155, published on 24.2.1982.

This patent claims in particular the stabilization of polyurethanes with mixtures consisting of esters of 2,2,6,6-tetramethyl-4-piperidinol, oxides or hydroxides of Mg or Zn and organic phosphites.

These mixtures do not give satisfactory results if they are used for the stabilization of polypropylene fibres.

On the other hand, British Patent 2,132,621 has reported the use of mixtures of ZnO and esters of 2,2,6,6-tetramethyl-4-piperidinol as photodegrading agents for polyolefins, in particular polyethylene and polypolypropylene.

European Patent 290,386 relates to the stabilisation of organic polymers by means of mixtures of salts and oxides of Zn/Mg with polyesters of the formula



in which R is hydrogen or methyl, A is a direct bond or C₂-C₁₀alkylene and n is an integer from 2 to 50.

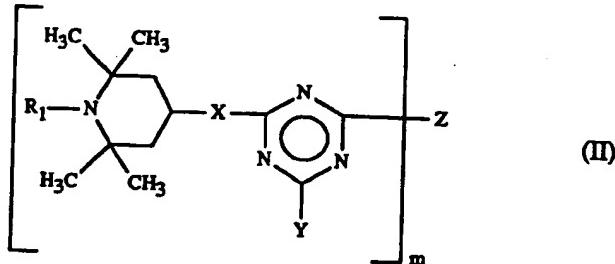
These mixtures do not show any synergistic effect on polypropylene in fibre form.

15 In European Patent 290,388, the use of oxides and hydroxides of Al, Mg and Zn in a mixture with compounds containing groups of the formula (I) for the light stabilisation of polyethylene is claimed.

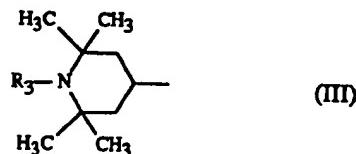
It has now been found, surprisingly, that mixtures analogous to those above are highly effective also in the light stabilisation of polypropylene, particularly in fibre form.

The compounds containing groups of the formula (I), which can be used according to the present invention, are:

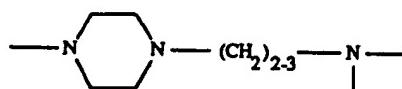
20 a) compounds of the general formula (II)



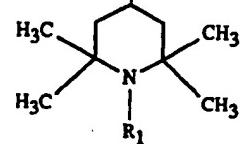
35 in which R₁ is as defined above for R, X is -O- or >N-R₂ where R₂ is hydrogen, C₁-C₁₈alkyl, C₂-C₄alkyl substituted in the 2-, 3- or 4-position by OH, by C₁-C₈alkoxy, by di-(C₁-C₄alkyl)amino or by a 5- to 7-membered nitrogenous heterocyclic group with the free valency on the nitrogen atom, C₆-C₁₂cycloalkyl, C₇-C₉phenylalkyl, tetrahyd-rofurfuryl or a group of the formula (III)



where R₃ is as defined for R, or X is 1,4-piperazinediyi or a group of the formula (IVa) or (IVb).

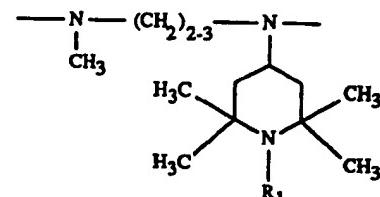


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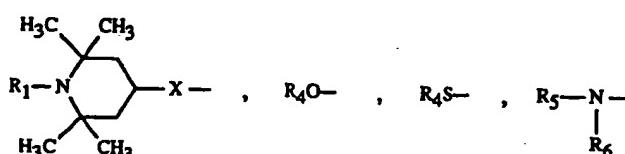
(Ty_a)



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with R₁ being as defined above and with the nitrogen atom substituted by the piperidyl group being bound to the triazine ring. Y is one of the groups:

15



25 In which R₁ and X are as defined above and R₄, R₅ and R₆ which can be identical or different are as defined for R₂ with the exception of the definition as a group of the formula (III), or they are C₃-C₁₈alkenyl or phenyl which is unsubstituted or mono-, di- or tri-substituted by C₁-C₆alkyl or C₁-C₆alkoxy, or

R₅ is a 5- to 7-membered nitrogenous heterocyclic group, m is an integer from 1 to 6, and, if m is 1, Z is as defined for Y, and, if m is 2, 3, 4 or 5, Z is one of the groups of the formulae (21) to (25).

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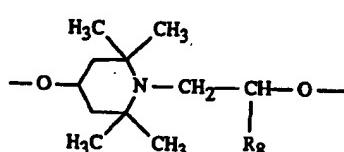


is a 5- to 7-membered nitrogenous heterocyclic group, m is an integer from 1 to 6, and, if m is 1, Z is as defined for Y, and, if m is 2, Z is one of the groups of the formulae A₁(n), A₂(n).

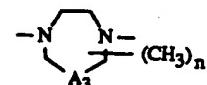
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(Va)



(Vb)



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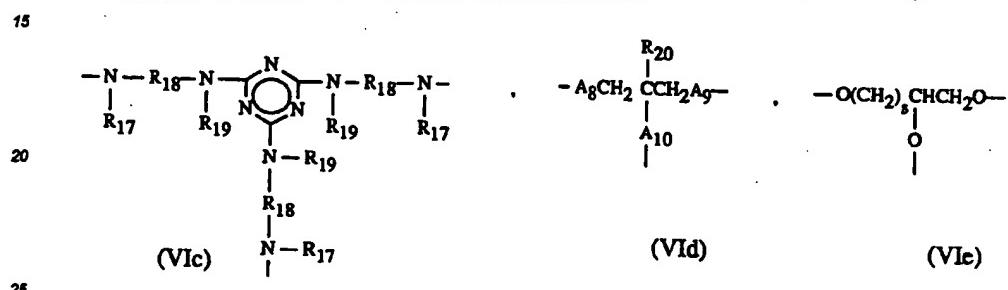
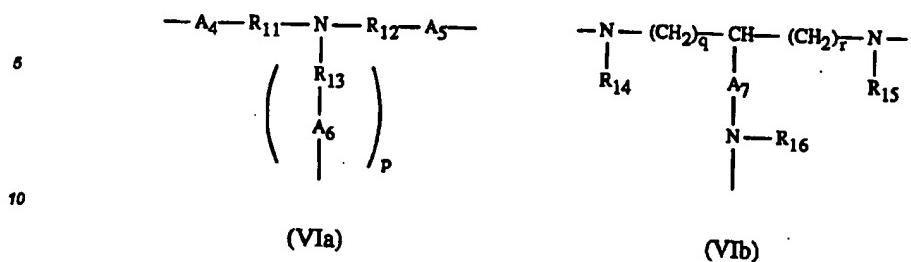
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in which A₁ and A₂ which can be identical or different are -O- or >N-R₉ with R₉ being hydrogen, C₁-C₁₈alkyl, C₅-C₁₂cycloalkyl, C₇-C₉phenylalkyl or a group of the formula (III), R₇ is C₂-C₁₂alkylene, cyclohexylene, cyclohexylenedimethylene, methylenedicyclohexylene, isopropylidenedicyclohexylene, phenylene, isopropylidenediphenylene, xylylene or C₄-C₁₂alkylene interrupted by 1, 2 or 3 oxygen atoms or by 1 or 2 >N-R₁₀ groups where R₁₀ is C₁-C₁₈alkyl, C₅-C₁₂cycloalkyl, C₇-C₉phenylalkyl or a group of the formula (III) or, if A₁ and A₂ both are >N-R₉, R₁₀ can also be hydrogen, C₁-C₈acyl or (C₁-C₈alkoxy)-carbonyl, or R₇ or A₁R₇, respectively are 8

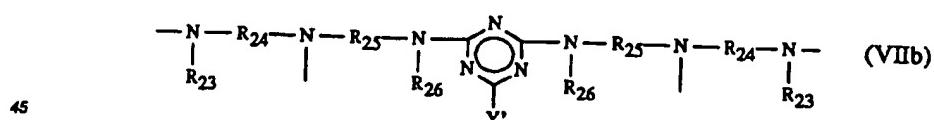
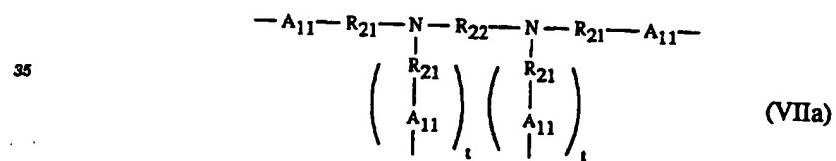
group — $(CH_2)_{2-3}-N$ N — $(CH_2)_{2-3}-$ or a group — N N — $(CH_2)_{2-3}-$ R₉ is

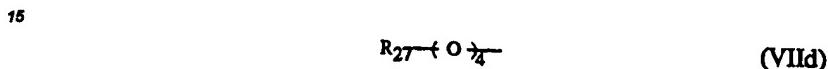
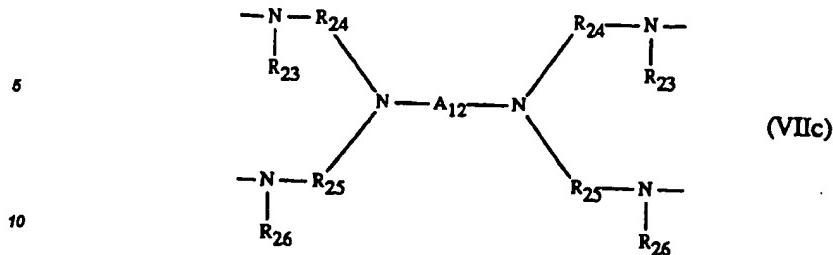
C₁-C₆alkyl, A₃ is a direct bond or -CH₂- and n is zero, 1, 2 or 3, and if m is 3, Z is one of the groups of the

formulae (Vla)-(Vle)

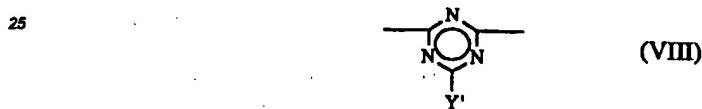


In which A₄, A₅, A₆, A₈, A₉ and A₁₀ which can be identical or different are as defined above for A₁ and A₂, and, if A₈ and A₉ both are -O-, A₁₀ can also be a -CH₂O- group, R₁₁, R₁₂, R₁₃ and R₁₈ which can be identical or different are C₂-C₆alkylene, p is zero or 1, R₁₄, R₁₅, R₁₆, R₁₇ and R₁₉ which can be identical or different are as defined above for R₆, A₇ is a direct bond or -CH₂, q, r and s which can be identical or different are integers from 2 to 6 and R₂₀ is hydrogen or C₁-C₆alkyl, and, if m is 4, Z is one of the groups of the formulae (VIIa)-(VIId)

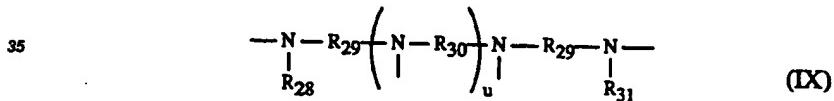




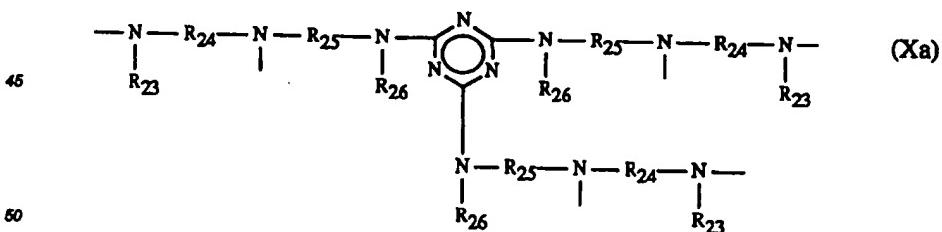
- 20 In which A₁₁ is as defined above for A₁ and A₂, R₂₁, R₂₂, R₂₄ and R₂₆ which can be identical or different are C₂-C₆alkylene, t is zero or 1, R₂₃ and R₂₅ which can be identical or different are as defined above for R₉, Y' is as defined for Y, A₁₂ is 2-hydroxytrimethylene, -CH₂CO-, xylylene, aliphatic or aromatic diacyl having not more than 12 carbon atoms, a group -COO(CH₂)₄₋₆OOC- or a group of the formula (VIII)

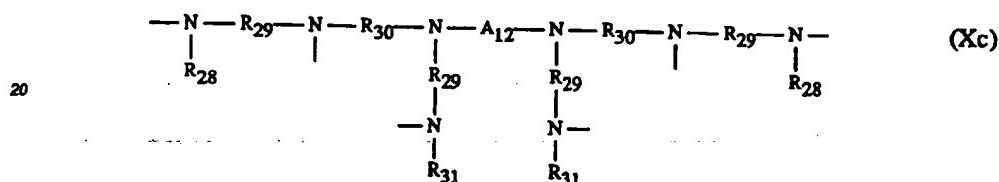
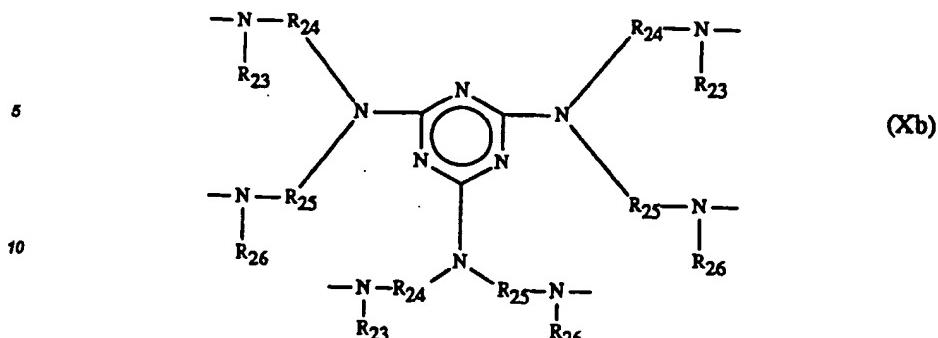


- 30 where Y' is as defined above, and R₂₇ is C₄-C₁₂alkanetetrayl, and, if m is 5 or 6, Z is a group of the formula (IX)

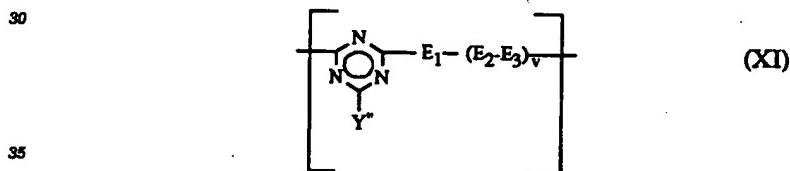


- 40 In which R₂₈ and R₃₁ which can be identical or different are as defined above for R₉, R₂₉ and R₃₀ which can be identical or different are C₂-C₆alkylene and u is 2 or 3, and, if m is 6, Z is also a group of the formulae (Xa)-(Xc)

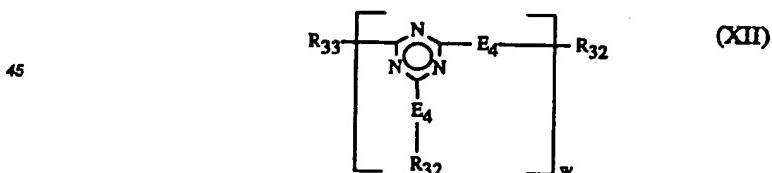




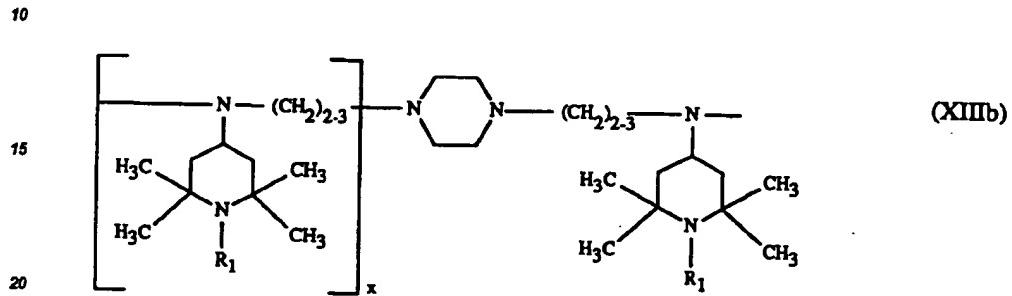
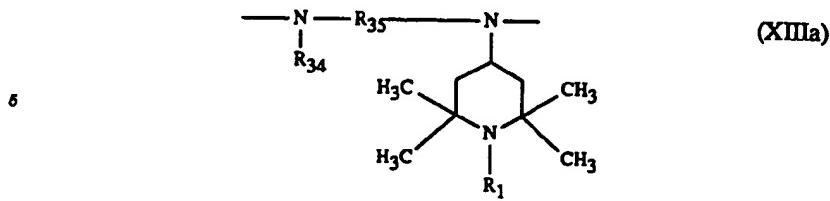
with R_{23} , R_{24} , R_{25} , R_{26} , R_{28} , R_{29} , R_{30} , R_{31} and A_{12} being as defined above;
b) oligomers having a molecular weight between 1,000 and 10,000 and containing recurring units of the formula (XI)



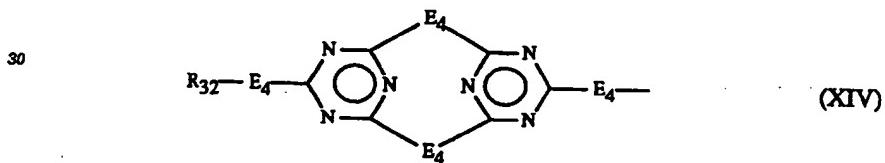
in which Y'' is as defined above for Y , E_1 and E_3 which can be identical or different are groups of the formulae (Va)-(Vc), E_2 is as defined above for A_{12} and v is zero, 1, 2, 3 or 4, with the proviso that at least one group of the formula (III) must be present in each recurring unit of the formula (XI);
c) oligomers of the formula (XII)



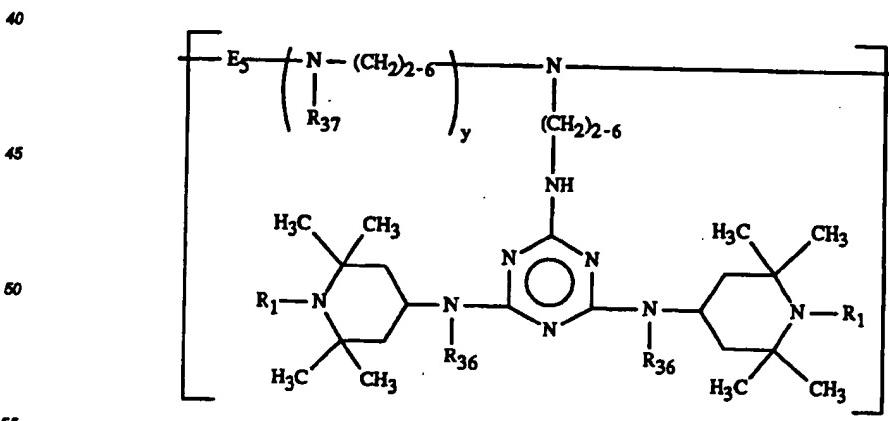
in which R_{32} is hydrogen, C_1-C_6 alkyl, C_3-C_6 alkenyl, C_7-C_8 phenylalkyl, C_1-C_6 acyl or $(C_1-C_6$ alkoxy)-carbonyl, E_4 is a group of the formula (XIIa) or (XIIb)



in which R₃₄ is as defined above for R₆, R₃₅ is C₂-C₁₂alkylene, cyclohexylene, cyclohexylenedimethylene,
25 methylenedicyclohexylene, xylylene or C₄-C₁₂alkylene interrupted by 1, 2 or 3 oxygen atoms or by a group >N-CH₃, R₁ is as defined above and x is zero or 1, R₃₃ is OH, ONa, OK, C₁-C₈alkoxy, C₃-C₈alkenyloxy, C₇-C₉phenylalkoxy, C₁-C₈acyloxy, a group R₃₂-E₄- or a group of the formula (XIV)

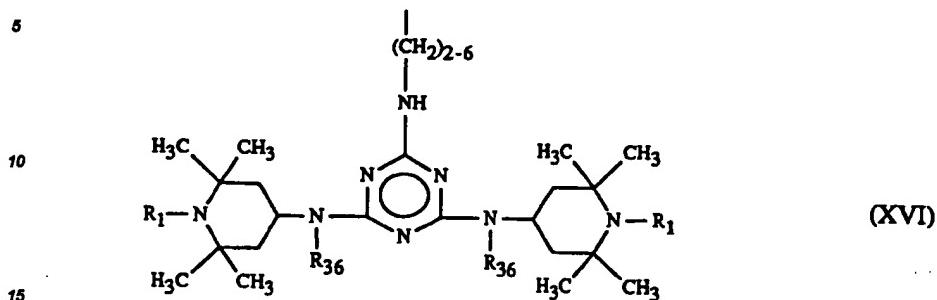


35 and w is a number from 1 to 20;
d) oligomers having a molecular weight between 1,000 and 10,000 and containing recurring units of the formula (XV)



(XV)

in which R₁ is as defined above, R₃₈ is as defined above for R₂, R₃₇ is hydrogen, C₁-C₁₈alkyl, a group of the formula (III) or a group of the formula (XVI)



y is zero or 1 and E₅ is as defined above for E₂ or C₂-C₆alkylene.

Examples of alkyl having not more than 18 carbon atoms are methyl, ethyl, propyl, isopropyl, butyl, 2-butyl, isobutyl, t-butyl, pentyl, 2-pentyl, hexyl, heptyl, octyl, 2-ethylhexyl, t-octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, hexadecyl and octadecyl.

20 Alkyl having not more than 12 carbon atoms is preferred.

Examples of C₂-C₄alkyl substituted by OH in the 2-, 3- or 4-position are 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, 2-hydroxybutyl and 4-hydroxybutyl.

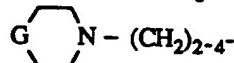
25 Examples of C₂-C₄alkyl substituted by C₁-C₈alkoxy in the 2-, 3- or 4-position are 2-methoxyethyl, 2-ethoxyethyl, 3-methoxypropyl, 3-ethoxypropyl, 3-butoxypropyl, 3-octoxypropyl and 4-methoxybutyl.

3-Methoxypropyl and 3-ethoxypropyl are preferred.

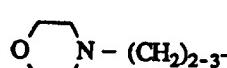
Examples of C₂-C₄alkyl substituted by di(C₁-C₄alkyl)amino in the 2-, 3- or 4-position are 2-dimethylaminoethyl, 2-diethylaminoethyl, 3-dimethylaminopropyl, 3-diethylaminopropyl, 3-dibutylaminopropyl and 4-diethylaminobutyl.

30 3-Dimethylaminopropyl and 3-diethylaminopropyl are preferred.

Representative examples of C₂-C₄alkyl R₂ substituted in the 2-, 3- or 4-position by a 5- to 7-membered nitrogenous heterocyclic group are groups of the formula



in which G is a direct bond, -O-, -CH₂- or -CH₂-CH₂.



45 is preferred.

Examples of alkoxy having not more than 8 carbon atoms are methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, t-butoxy, pentoxy, isopentoxy, hexoxy, heptoxy and octoxy.

C₆-C₈alkoxy and in particular heptoxy and octoxy are preferred for R₁ and R₃.

50 Representative examples of C₆-C₈cycloalkoxy R₁ and R₃ are cyclopentyx, cyclohexoxy, cycloheptoxy and cyclooctoxy.

Cyclopentyx and cyclohexoxy are preferred.

The various C₅-C₁₂cycloalkyl substituents are unsubstituted or mono-, di- or tri-substituted by C₁-C₄alkyl; representative examples are cyclopentyl, methylcyclopentyl, dimethylcyclopentyl, cyclohexyl, methylcyclohexyl, dimethylcyclohexyl, trimethylcyclohexyl, t-butylcyclohexyl, cyclooctyl, cyclodetyl and cyclododecyl. Cyclohexyl is preferred.

55 Examples of alkenyl having not more than 18 carbon atoms are allyl, 2-methylallyl, butenyl, pentenyl, hexenyl, undecenyl and oleyl. Alkenyl groups in which the carbon atom in the 1-position is saturated are preferred; allyl is particularly preferred.

Examples of substituted phenyl are methylphenyl, dimethylphenyl, trimethylphenyl, t-butylphenyl, di-t-butylphenyl, methoxyphenyl and ethoxyphenyl.

The various C₇-C₉phenylalkyl substituents are unsubstituted or mono-, di- or tri-substituted on the phenyl by C₁-C₄alkyl; representative examples are benzyl, methylbenzyl, dimethylbenzyl, t-butylbenzyl and 2-phenylethyl. Benzyl is preferred.

Acyl R₁, R₃ and R₁₀ having not more than 8 carbon atoms can be an aliphatic or aromatic group.

Representative examples are formyl, acetyl, propionyl, butyryl, pentanoyl, hexanoyl, heptanoyl, octanoyl, benzoyl, acryloyl or crotonyl. Acetyl is preferred.

A

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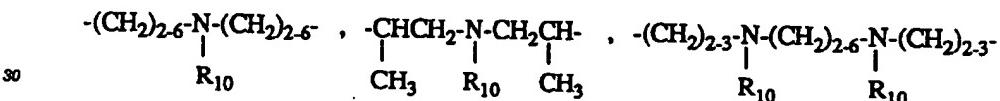
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group as a 5- to 7-membered heterocyclic group can contain a further hetero atom, for example nitrogen or oxygen; representative examples are 1-pyrrolidyl, 1-piperidyl, 4-morpholinyl, 4-methyl-1-piperazinyl and 1-hexahydroazepinyl. 4-Morpholinyl is preferred.

Examples of alkylene having not more than 12 carbon atoms are ethylene, propylene, trimethylene, tetramethylene, pentamethylene, 2,2-dimethyltrimethylene, hexamethylene, trimethylhexamethylene, octamethylene, decamethylene and dodecamethylene.

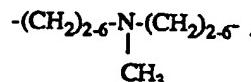
Examples of C₄-C₁₂alkylene interrupted by 1, 2 or 3 oxygen atoms are 3-oxapentane-1,5-diyl, 4-oxahexane-1,7-diyl, 3,6-dioxaoctane-1,8-diyl, 4,7-dioxadecane-1,10-diyl, 4,9-dioxadodecane-1,12-diyl and 3,6,9-trioxaundecane-1,11-diyl.

25 Representative examples of C₄-C₁₂alkylene R₇ interrupted by 1 or 2 >N-R₁₀ groups are the groups



A representative example C₄-C₁₂alkylene R₃₈ interrupted by an >N-CH₃ group of the formula

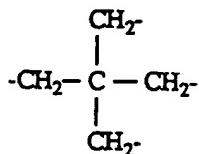
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40 Examples of diacyl A₁₂ having not more than 12 carbon atoms are oxallyl, malonyl, succinyl, glutaryl, adipoyl, sebacoyl, isophthaloyl and terephthaloyl.

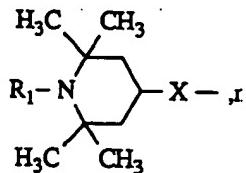
Preferred examples of C₄-C₁₂alkanetetrayl R₂₇ are 1,2,3,4-butanetetrayl and the group

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Preferred compounds containing groups of the formula (I), which can be used according to the present invention, are those of the formula (I) in which R₁ is hydrogen, methyl, allyl, benzyl or acetyl, X is -O- or >N-R₂, R₂ is hydrogen, C₁-C₁₂alkyl, C₂-C₃alkyl substituted in the 2- or 3-position by C₁-C₄alkoxy, by diethylamino, by diethylamino or by 4-morpholinyl, cyclohexyl, benzyl, tetrahydrofuryl or a group of formula (III) with R₃ being as defined above for R₁, Y is a group



m is an integer from 2 to 6 and, if m is 2, Z is a group of the formula (Va) in which A₁ and A₂ are >N-R₆ with R₆ being hydrogen, C₁-C₁₂alkyl, cyclohexyl, benzyl or a group of the formula (III), R₇ is C₂-C₆alkylene, cyclohexylenedimethylene, methylenedicyclohexylene, xylylene or C₄-C₁₀alkylene interrupted by 1 or 2 oxygen atoms or by 1 or 2 >N-R₁₀ groups where R₁₀ is hydrogen, C₁-C₁₂alkyl, cyclohexyl, benzyl, a group of the formula (III), C₁-C₄acyl or (C₁-C₄alkoxy)-carbonyl, or Z is a group



20 and, if m is 3, Z is a group of the formula (Vla) in which A₄ and A₅ are as defined above for A₁ and A₂, R₁₁ and R₁₂ which can be identical or different are C₂-C₆alkylene and p is zero, and, if m is 4, Z is a group of the formula (VIIa) or (VIIc) in which A₁₁ is as defined above for A₁ and A₂, R₂₁, R₂₂, R₂₄ and R₂₅ which can be identical or different are C₂-C₆alkylene, t is zero, R₂₃ and R₂₆ are as defined above for R₉ and A₁₁ is aliphatic or aromatic
25 diacyl having not more than 10 carbon atoms or a group -COO(CH₂)₄₋₆OOC, and, if m is 5 or 6, Z is a group of the formula (IX) in which R₂₈ and R₃₁ are as defined above for R₉, R₂₉ and R₃₀ which can be identical or different are C₂-C₆alkylene and u is 2 or 3, and, if m is 6, Z is also a group of the formula (Xc) with R₂₈, R₂₉, R₃₀, R₃₁ and A₁₂ being as defined above; oligomers having a molecular weight between 1,000 and 5,000 and containing recurring units of the formula (XI) in which Y" is one of the groups



R₄O- and



where R₁ and X are as defined above, and R₄, R₅ and R₆ which can be identical or different are as defined above for R₂, or

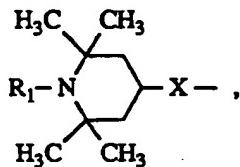


55 is 4-morpholinyl, E₁ and E₃ which can be identical or different are groups of the formulae (Va)-(Vc) where A₁, A₂ and R₇ are as defined above, R₈ is hydrogen or methyl, A₃ is a direct bond and n is zero, E₂ is 2-hydroxy-
trimethylene, aliphatic or aromatic diacyl having not more than 10 carbon atoms, a group -COO(CH₂)₄₋₆OOC-

or a group of the formula (VIII) where Y' is as defined for Y" and v is zero, 1 or 2, with the proviso that at least one group of the formula (III) must be present in each recurring unit of the formula (XI); oligomers of the formula (XII) in which R₃₂ is hydrogen, C₁-C₄alkyl, C₁-C₄acyl or (C₁-C₄alkoxy)-carbonyl, E₄ is a group of the formula (XIIIa) or (XIIIb) in which R₃₄ is as defined above for R₆, R₃₅ is C₂-C₆alkylene, cyclohexylenedimethylene, methylenedicyclohexylene or C₄-C₁₀alkylene interrupted by 1 or 2 oxygen atoms or by an >N-CH₃ group, R₁ is as defined above and x is zero or 1, R₃₃ is OH, ONa, OK, C₁-C₄alkoxy, C₁-C₄acyloxy, a group R₃₂-E₄- or a group of the formula (XIV) and w is a number from 1 to 10; oligomers having a molecular weight between 1000 and 5000 and containing recurring units of the formula (XV) in which R₁ is as defined above, R₃₈ is as defined above for R₂, R₃₇ is hydrogen, C₁-C₁₂alkyl, a group of the formula (III) or a group of the formula (XVI), y is 1 and E₅ is as defined above for E₂ or C₂-C₆alkylene.

Particularly preferred compounds containing groups of the formula (I), which can be used according to the present invention are a) those of the formula (II) in which R₁ is hydrogen or methyl, X is >N-R₂, R₂ is C₁-C₆alkyl, 2,2,6,6-tetramethyl-4-piperidyl or 1,2,2,6,6-pentamethyl-4-piperidyl, Y is a group

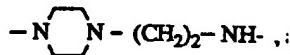
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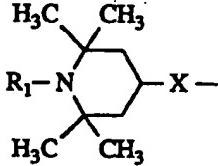
m is 2, 3 or 4 and, if m is 2, Z is a group of the formula (Va) in which A₁ and A₂ are >N-R₉ with R₉ being hydrogen, C₁-C₄alkyl, 2,2,6,6-tetramethyl-4-piperidyl, or : 1,2,2,6,6-pentamethyl-4-piperidyl, R₇ is C₂-C₆alkylene, cyclohexylenedimethylene, methylenedicyclohexylene, xylylene or C₄-C₁₀alkylene interrupted by 1 or 2 oxygen atoms or by an >N-R₁₀ group where R₁₀ is hydrogen, methyl, cyclohexyl, benzyl, C₁-C₄acyl or (C₁-C₄alkoxy)-carbonyl, or Z is a group

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and, if m is 3, Z is a group of the formula (Via) in which A₄ and A₆ are as defined above for A₁ and A₂, R₁₁ and R₁₂ which can be identical or different are C₂-C₆alkylene and p is zero, and, if m is 4, Z is a group of the formula (VIIa) or (VIIc) in which A₁₁ is as defined above for A₁ and A₂, R₂₁, R₂₂, R₂₄ and R₂₆ which can be identical or different, are C₂-C₆alkylene, t is zero, R₂₃ and R₂₅ are as defined above for R₆ and A₁₂ is aliphatic C₂-C₁₀diacyl or a group -COO(CH₂)₄₋₆OOC-; b) oligomers having a molecular weight between 1,500 and 5,000 and containing recurring units of the formula (XI) in which Y" is one of the groups

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or

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where R₅ and X are as defined above and R₆ and R₈ which can be identical or different are C₁-C₆alkyl, or R₆

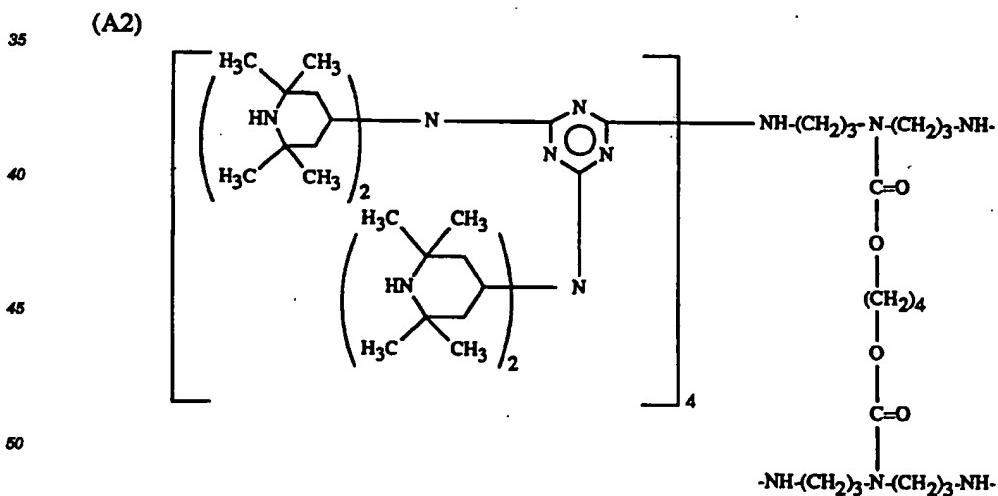
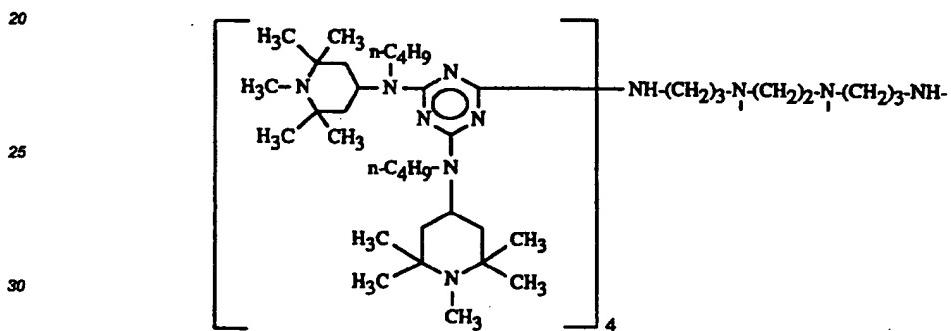
can also be hydrogen, or



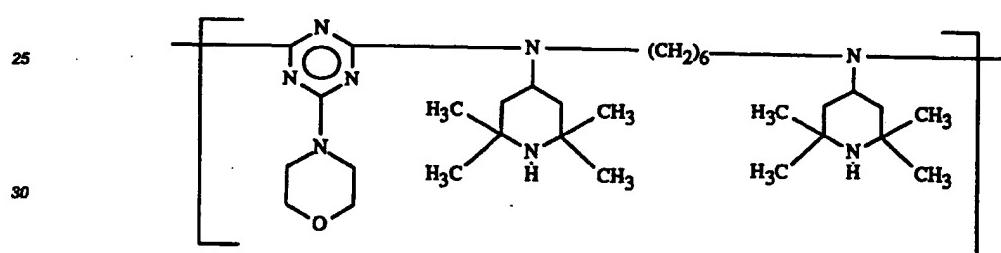
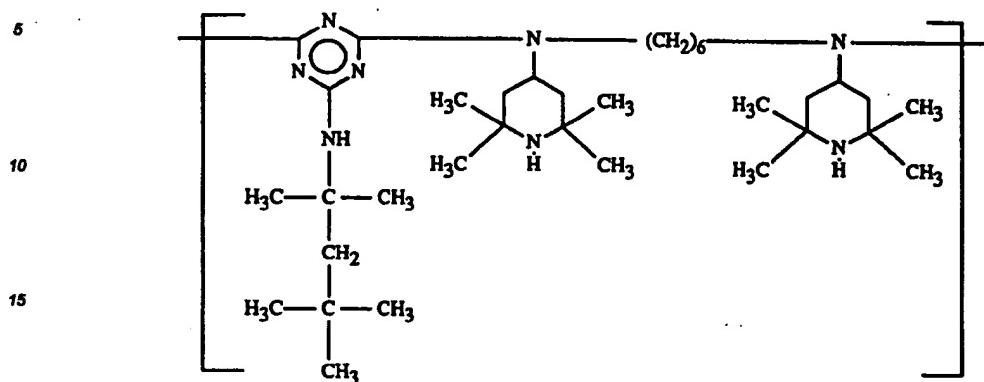
is 4-morpholinyl, E_1 is a group of the formula (Va) as defined above and v is zero, with the proviso that at least one group of the formula (III) must be present in each recurring unit of the formula (XI); c) oligomers of the formula (XII) in which R_{32} is hydrogen, methyl, acetyl or ($\text{C}_1\text{-C}_2$ -alkoxy)-carbonyl, E_4 is a group of the formula (XIIia) in which R_{34} is 2,2,6,6-tetramethyl-4-piperidyl or 1,2,2,6,6-pentamethyl-4-piperidyl, R_{35} is $\text{C}_2\text{-C}_6$ -alkylene or $\text{C}_6\text{-C}_{10}$ -alkylene interrupted by 2 oxygen atoms, R_1 is as defined above, R_{33} is a group $\text{R}_{32}\text{-E}_4-$ or a group of the formula (XIV) and w is a number from 1 to 5; oligomers having a molecular weight between 1,500 and 5,000 and containing recurring units of formula (XV) in which R_1 is as defined above, R_{36} is as defined above for R_2 , R_{37} is hydrogen or a group of the formula (XVI), y is 1 and E_6 is $\text{C}_2\text{-C}_6$ -alkylene.

10 Compounds A) of particular interest, which can be used according to the present invention are:

A1)



A3) oligomers having a molecular weight between 1,500 and 4,000 and containing recurring units of the formula



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A5) oligomers having a molecular weight between 1,500 and 4,000 and containing recurring units of the formula

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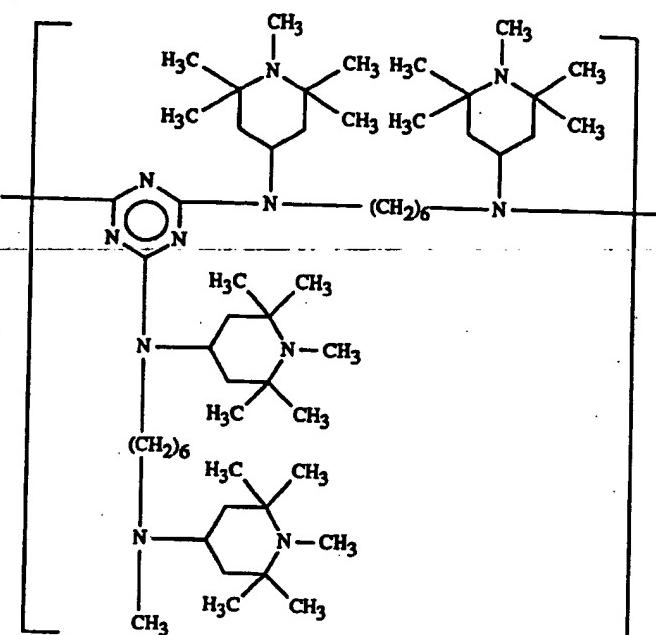
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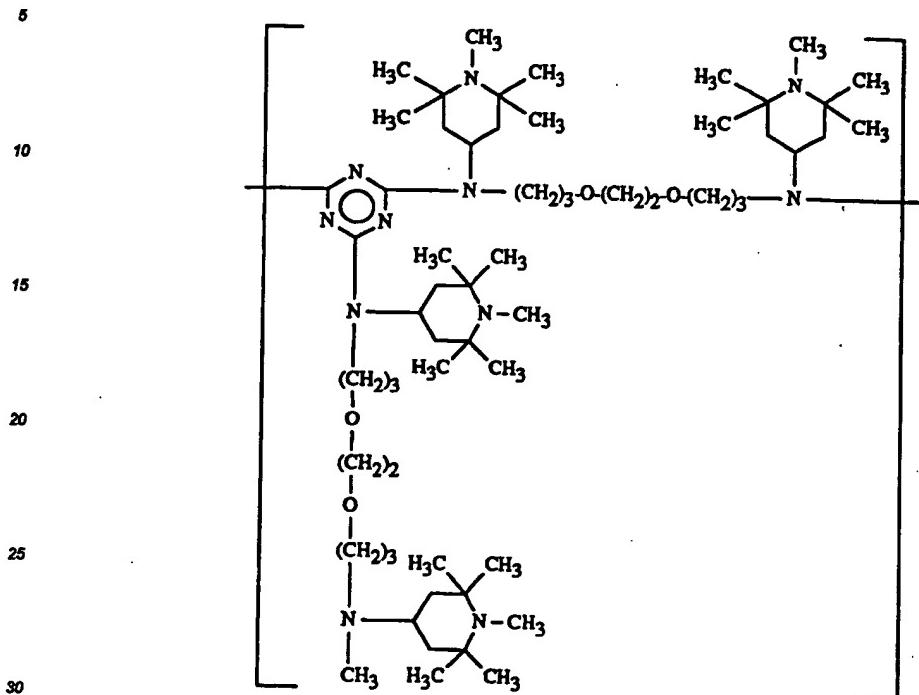
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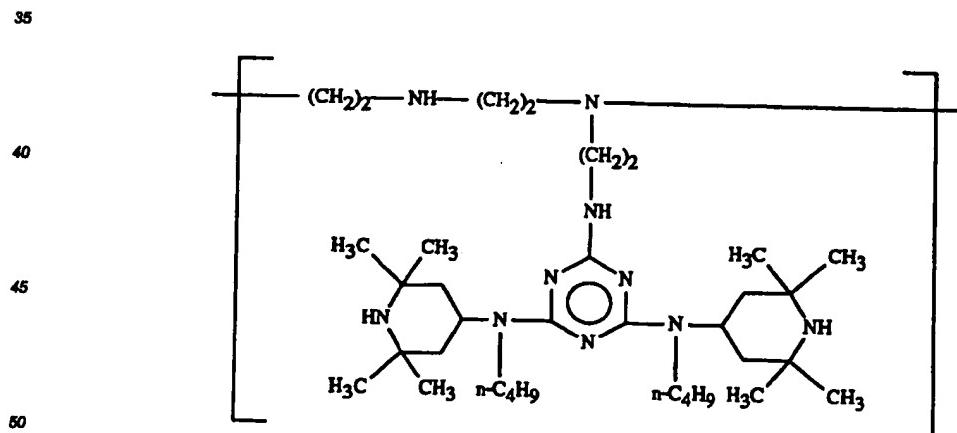
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A6) oligomers having a molecular weight between 1,500 and 4,000 and containing recurring units of the formula



A7) oligomers having a molecular weight between 1,500 and 4,000 and containing recurring units of the formula



The said compounds can be used alone or as a mixture with one another.

The compounds (B) which can be used according to the present invention are preferably the oxides and hydroxides of Mg and Zn. The oxides of Mg and Zn are particularly preferred, and they can be used alone or as a mixture with one another. The weight ratio of A:B is preferably from 1:0.1 to 1:2.

The percentages by weight, relative to the weight of the polypropylene, of the compounds (A) and (B) which can be used according to the present invention are between 0.025 and 2 %, preferably between 0.05 and 1 %.

for the compounds (A) and between 0.005 and 1 %, preferably between 0.025 and 0.5 %, for the compounds (B).

The compounds (A) and (B) can be mixed with one another before the addition to the polymer, or they can be added separately to the polymer, using any of the known procedures.

In addition to the compounds (A) and (B) of the present invention, other conventional additives for polypolypropylene, such as antioxidants, UV absorbers, nickel stabilisers, pigments, fillers, antistatic agents, flameproofing agents, lubricants, corrosion inhibitors and metal deactivators, can be added.

Particular examples of additives which can be used in admixture with the compounds (A) and (B) are:

10 1. Antioxidants

1.1. Alkylated monophenols, for example 2,6-di-tert-butyl-4-methylphenol, 2-tert-butyl-4,6-dimethylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butyl-4-n-butylphenol, 2,6-di-tert-butyl-4-isobutylphenol, 2,6-dicyclopentyl-4-methylphenol, 2-(α -methylcyclohexyl)-4,6-dimethylphenol, 2,6-dioctadecyl-4-methylphenol, 2,4,6-tricyclohexylphenol, 2,6-di-tert-butyl-4-methoxymethylphenol, 2,6-dinonyl-4-methylphenol.

1.2. Alkylated hydroquinones, for example 2,6-di-tert-butyl-4-methoxyphenol, 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amylhydroquinone, 2,6-diphenyl-4-octadecyloxyphephenol.

1.3. Hydroxylated thioldiphenyl ethers, for example 2,2'-thiobis(6-tert-butyl-4-methylphenol), 2,2'-thiobis(4-octylphenol), 4,4'-thiobis(6-tert-butyl-3-methylphenol), 4,4'-thiobis(6-tert-butyl-2-methylphenol).

1.4. Alkyldenebisphenols, for example 2,2'-methylenebis(6-tert-butyl-4-methylphenol), 2,2'-methylenebis(6-tert-butyl-4-ethylphenol), 2,2'-methylenebis[4-methyl-6-(α -methylcyclohexyl)phenol], 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,2'-methylenebis(6-nonyl-4-methylphenol), 2,2'-methylenebis(4,6-di-tert-butylphenol), 2,2'-ethyldenebis(4,6-di-tert-butylphenol), 2,2'-ethyldenebis(6-tert-butyl-4-isobutylphenol), 2,2'-methylenebis[6-(α -methylbenzyl)-4-nonylphenol], 2,2'-methylenebis[6-(α , α -dimethylbenzyl)-4-nonylphenol], 4,4'-methylenebis(2,6-di-tert-butylphenol), 4,4'-methylenebis(6-tert-butyl-2-methylphenol), 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 2,6-bis(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol, 1,1,3-tris(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-3-n-dodecylmercaptobutane, ethylene glycol bis[3,3-bis(3'-tert-butyl-4'-hydroxyphenyl)butyrate], bis(3-tert-butyl-4-hydroxy-5-methylphenyl)-dicyclopentadiene, bis[2-(3'-tert-butyl-2'-hydroxy-5'-methylbenzyl)-6-tert-butyl-4-methylphenyl] terephthalate.

1.5. Benzyl compounds, for example 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, bis(3,5-di-tert-butyl-4-hydroxybenzyl) sulfide, isoctyl 3,5-di-tert-butyl-4-hydroxybenzylmercaptoacetate, bis(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl) dithiolterephthalate, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl) isocyanurate, 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl) isocyanurate, dioctadecyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate, calcium salt of monoethyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate, 1,3,5-tris(3,5-dicyclohexyl-4-hydroxybenzyl) isocyanurate.

1.6. Acylaminophenols, for example lauric acid 4-hydroxyanilide, stearic acid 4-hydroxyanilide, 2,4-bis(octylmercapto)-6-(3,5-di-tert-butyl-4-hydroxyanilino)-s-triazine, octyl N-(3,5-di-tert-butyl-4-hydroxyphenyl)-carbamate.

1.7. Esters of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, diethylene glycol, octadecanol, triethylene glycol, 1,6-hexanediol, pentaerythritol, neopentyl glycol, tris(hydroxyethyl) isocyanurate, thiodiethylene glycol, N,N'-bis(hydroxyethyl)oxamide.

1.8. Esters of β -(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, diethylene glycol, octadecanol, triethylene glycol, 1,6-hexanediol, pentaerythritol, neopentyl glycol, tris(hydroxyethyl) isocyanurate, thiodiethylene glycol, N,N'-bis(hydroxyethyl)oxamide.

1.9. Esters of β -(3,5-dicyclohexyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, diethylene glycol, octadecanol, triethylene glycol, 1,6-hexanediol, pentaerythritol, neopentyl glycol, tris(hydroxyethyl) isocyanurate, thiodiethylene glycol, N,N'-bis(hydroxyethyl)oxamide.

1.10. Amides of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid e.g. N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexamethylenediamine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)trimethylene diamine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazine.

2. UV absorbers and light stabilisers

2.1. 2-(2'-Hydroxyphenyl)benzotriazoles, for example the 5'-methyl, 3',5'-di-tert-butyl, 5'-tert-butyl, 5'-(1,1,3,3-tetramethylbutyl), 5-chloro-3',5'-di-tert-butyl, 5-chloro-3'-tert-butyl-5'-methyl, 3'-sec-butyl-5'-tert-butyl, 4'-octoxy, 3',5'-di-tert-amyl and 3',5'-bis(α , α -dimethylbenzyl) derivatives.

2.2. 2-Hydroxybenzophenones, for example the 4-hydroxy, 4-methoxy, 4-octoxy, 4-decyloxy, 4-dodecy-

loxy, 4-benzyloxy, 4,2',4'-trihydroxy and 2'-hydroxy-4,4'-dimethoxy derivatives.

2.3. Esters of variously substituted benzoic acids, for example 4-tert-butylphenyl salicylate, phenyl salicylate, octylphenyl salicylate, dibenzoylresorcinol, bis (4-tert-butylbenzoyl)resorcinol, benzoylresorcinol, 2,4-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate and hexadecyl 3,5-di-tert-butyl-4-hydroxybenzoate.

2.4. Acrylates, for example ethyl α -cyano- β,β -diphenylacrylate, isoctyl α -cyano- β,β -diphenylacrylate, methyl α -carbomethoxycinnamate, methyl α -cyano- β -methyl- ρ -methoxycinnamate, butyl α -cyano- β -methyl- ρ -methoxycinnamate, methyl α -carbomethoxy- ρ -methoxycinnamate and N-(β -carbomethoxy- β -cyanovinyl)-2-methylindoline.

2.5. Nickel compounds, for example nickel complexes of 2,2'-thiobis[4-(1,1,3,3-tetramethylbutyl)phenol], such as the 1:1 or 1:2 complex, with or without additional ligands such as n-butylamine, triethanolamine or N-cyclohexyl diethanolamine, nickel dibutylidithiocarbamate, nickel salts of 4-hydroxy-3,5-di-tert-butylbenzyl phosphonic acid monoalkyl esters, e.g. of the methyl or ethyl ester, nickel complexes of ketoximes, e.g. of 2-hydroxy-4-methylphenyl undecyl ketoxime, nickel complexes of 1-phenyl-4-lauryl-5-hydroxypyrazole, with or without additional ligands.

2.6. Oxalic acid diamides, for example, 4,4'-dioctyloxoxanilide, 2,2'-dioctyloxy-5,5'-di-tert-butylloxanilide, 2,2'-didodecyloxy-5,5'-di-tert-butylloxanilide, 2-ethoxy-2'-ethyloxanilide, N,N'-bis(3-dimethylaminopropyl)oxamide, 2-ethoxy-5-tert-butyl-2'-ethyloxanilide and its mixtures with 2-ethoxy-2'-ethyl-5,4'-di-tert-butylloxanilide and mixtures of ortho- and para-methoxy-disubstituted oxanilides and mixtures of o- and p-ethoxy-disubstituted oxanilides.

2.7. 2-(2-Hydroxyphenyl)-1,3,5-triazines, for example 2,4,6-tris(2-hydroxy-4-octyloxyphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2,4-dihydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(4-methylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-dodecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine.

3. Metal deactivators, for example N,N'-diphenyloxamide, N-salicyyal-N'-salicyloylhyclazine, N,N'-bis(salicyloyl)hydrazine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazine, 3-salicyloylamino-1,2,4-triazole, bis(benzylidene)oxalodihydrazide.

4. Phosphites and phosphonites, for example triphenyl phosphite, diphenyl alkyl phosphites, phenyl dialkyl phosphites, tris(nonylphenyl) phosphite, triauryl phosphite, trioctadecyl phosphite, distearyl pentaerythritol diphosphate, tris(2,4-di-tert-butylphenyl) phosphite, diisodecyl pentaerythritol diphosphate, bis(2,4-di-tert-butylphenyl) pentaerythritol diphosphate, tristearyl sorbitol triphosphate, tetrakis(2,4-di-tert-butylphenyl) 4,4'-biphenylenediphosphonite, 3,9-bis(2,4-di-tert-butylphenoxy)-2,4,8, 10-tetraoxa-3,9-diphosphaspiro[5.5]undecane.

4a. Hydroxylamines, for example dibenzylhydroxylamine, dioctylhydroxylamine, didodecylhydroxylamine, ditetradecylhydroxylamine, dihexadecylhydroxylamine, dioctadecylhydroxylamine, 1-hydroxy-2,2,6,6-tetramethyl-4-piperidyl benzoate or bis-(1-hydroxy-2,2,6,6-tetramethyl-4-piperidyl) sebacate.

5. Peroxide scavengers, for example esters of β -thiodipropionic acid, for example the lauryl, stearyl, myristyl or tridecyl esters, mercaptobenzimidazole or the zinc salt of 2-mercaptobenzimidazole, zinc dibutylidithiocarbamate, dioctadecyl disulfide, pentaerythritol tetrakis(β -dodecylmercapto)propionate.

6. Polyamide stabilisers, for example copper salts in combination with iodides and/or phosphorus compounds and salts of divalent manganese.

7. Basic co-stabilisers, for example melamine, polyvinylpyrrolidone, dicyandiamide, triallyl cyanurate, urea derivatives, hydrazine derivatives, amines, polyamides, polyurethanes, alkali metal salts and alkaline earth metal salts of higher fatty acids, for example calcium stearate, zinc stearate, magnesium stearate, sodium ricinoleate and potassium palmitate, antimony pyrocatecholate or zinc pyrocatecholate.

8. Nucleating agents, for example 4-tert-butyl-benzoic acid, adipic acid, diphenylacetic acid.

9. Fillers and reinforcing agents, for example calcium carbonate, silicates, glass fibres, asbestos, talc, kaolin, mica, barium sulfate, metal oxides and hydroxides, carbon black, graphite.

10. Other additives, for example plasticizers, lubricants, emulsifiers, pigments, optical brighteners, flame-roofing agents, antistatic agents and blowing agents.

The use of the mixtures stabilised according to the present invention is illustrated by the examples which follow; these are given solely for illustrative purposes and do not imply any restriction.

EXAMPLES 1-7:

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2.5 g of each of the products indicated in Table 1, 1 g of tris-(2,4-di-tert-butylphenyl) phosphite, 0.5 g of calcium monoethyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate, 1 g of calcium stearate, 2.5 g of titanium dioxide and MgO or ZnO in the quantities indicated in the table are mixed in a slow mixer with 1000 g of polypropylene

powder of melt index = 12 g/10 minutes (measured at 230°C and 2.16 kg).

The mixtures are extruded at 200-230°C to give polymer granules which are then converted into fibres, using a pilot-type apparatus (Leonard, Sumirago (VA), Italy) operating under the following conditions:

5	Extruder temperature	: 200-230°C
	Head temperature	: 255-260°C
	Stretch ratio	: 1:3.5
10	Count	: 11 dtex per filament

The fibres thus prepared are exposed, mounted on a white card, in a model 65 WR Weather-O-Meter (ASTM G 26-77) with a black panel temperature of 63°C.

15 The residual tenacity is measured on samples taken after various times of exposure to light by means of a constant-speed tensometer, and the exposure time in hours (T50) needed to halve the initial tenacity is then calculated.

Fibres prepared under the same conditions as indicated above, but without addition of the compounds of the invention, are exposed for comparison.

20 The results obtained are shown in Table 1:

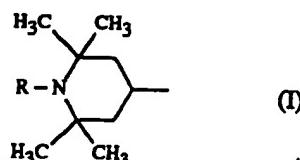
TABLE 1

Example No.	Compound (A)	Compound (B) (g)	T50 (hours)
25	1	-	1110
	2	MgO (1)	1600
30	3	MgO (2)	1700
	4	ZnO (1)	1480
35	5	-	1270
	6	MgO (2)	1600
	7	ZnO (1)	1790

40 Claims

1. A stabiliser composition for polypropylene, comprising:

45 A) one or more triazine compounds containing piperidine groups of the formula (I)



55 in which R is hydrogen, C₁-C₄alkyl, O-, OH, C₁-C₈alkoxy, C₅-C₈cycloalkoxy, C₃-C₆alkenyl, C₇-C₉phenylalkyl or C₁-C₈acyl, and

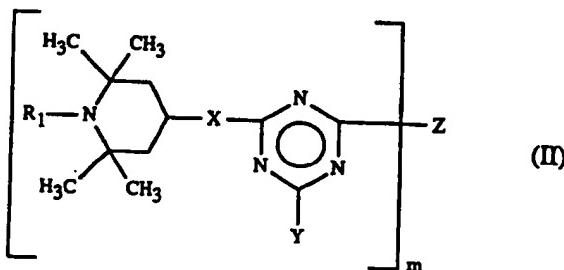
B) one or more oxides and hydroxides of Mg, Ca, Ba, Zn, Al and Sn.

2. A stabiliser composition according to claim 1, wherein the compound (A) containing groups of the formula (I) is selected from the group comprising
 a) compounds of the formula (II)

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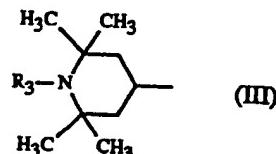
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In which R₁ is as defined above for R, X is -O- or >N-R₂ where R₂ is hydrogen, C₁-C₁₈alkyl, C₂-C₄alkyl substituted in the 2-, 3- or 4-position by OH, by C₁-C₈alkoxy, by di-(C₁-C₄alkyl)amino or by a 5- to 7-membered nitrogenous heterocyclic group with the free valency on the nitrogen atom, C₆-C₁₂cycloalkyl, C₇-C₉phenylalkyl, tetrahydrofurfuryl or a group of the formula (III)

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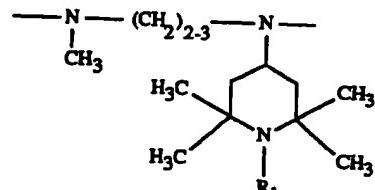
where R₃ is as defined for R, or X is 1,4-piperazinediyl or a group of the formula (IVa) or (IVb)

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(IVa)

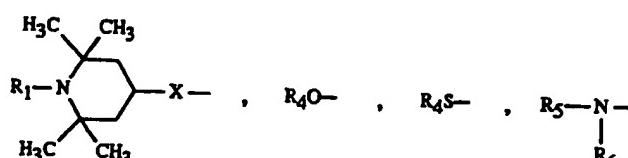
(IVb)



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with R₁ being as defined above and with the nitrogen atom substituted by the piperazinediyl group being bound to the triazine ring, Y is one of the groups

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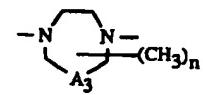
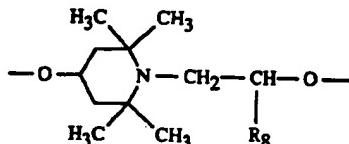
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In which R₁ and X are as defined above and R₄, R₅ and R₆ which can be identical or different are as defined for R₂ with the exception of the definition as a group of the formula (III), or they are C₃-C₁₈alkenyl or phenyl which is unsubstituted or mono-, di- or tri-substituted by C₁-C₄alkyl or C₁-C₄alkoxy, or



5

is a 5- to 7-membered nitrogenous heterocyclic group, m is an integer from 1 to 6, and, if m is 1, Z is as defined for Y, and, if m is 2, Z is one of the groups of the formulae (Va)-(Vc)



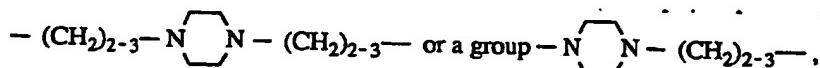
15 (Va)

(Vb)

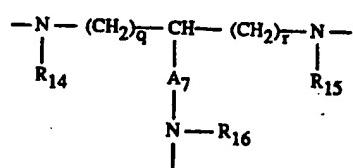
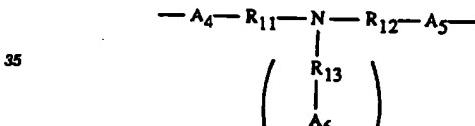
(Vc)

in which A_1 and A_2 which can be identical or different are $-\text{O}$ - or $>\text{N-R}_6$ with R_6 being hydrogen, $\text{C}_1\text{-C}_8$ alkyl, $\text{C}_5\text{-C}_{12}$ cycloalkyl, $\text{C}_7\text{-C}_9$ phenylalkyl or a group of the formula (III), R_7 is $\text{C}_2\text{-C}_{12}$ alkylene, cyclohexylene, cyclohexylenedimethylene, methylenedicyclohexylene, isopropylidenedicyclohexylene, phenylene, isopropylidenediphenylene, xylylene or $\text{C}_4\text{-C}_{12}$ alkylene interrupted by 1, 2 or 3 oxygen atoms or by 1 or 2 $>\text{N-R}_{10}$ groups where R_{10} is $\text{C}_1\text{-C}_{12}$ alkyl, $\text{C}_5\text{-C}_{12}$ cycloalkyl, $\text{C}_7\text{-C}_9$ phenylalkyl or a group of the formula (III) or, if A_1 and A_2 both are $>\text{N-R}_6$, R_{10} can also be hydrogen, $\text{C}_1\text{-C}_8$ acyl or $(\text{C}_1\text{-C}_8$ alkoxy)-carbonyl, or R_7 or A_1R_7 respectively are a group

25



30 R_8 is $\text{C}_1\text{-C}_8$ alkyl, A_3 is a direct bond or CH_2 and n is zero, 1, 2 or 3, and, if m is 3, Z is one of the groups of the formulae (VIa)-(VIe)

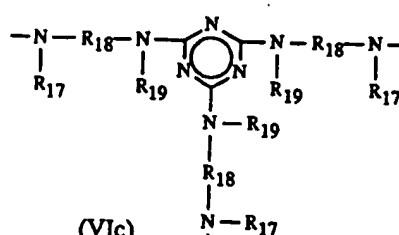


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(VIa)

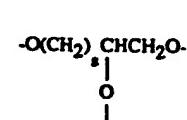
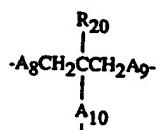
(VIb)

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(VIc)



(VID)

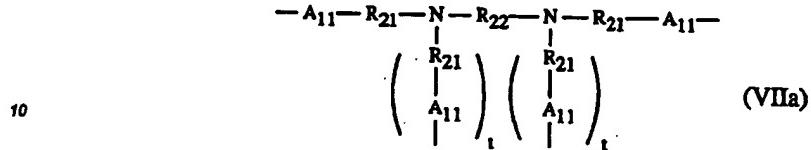
(VIe)

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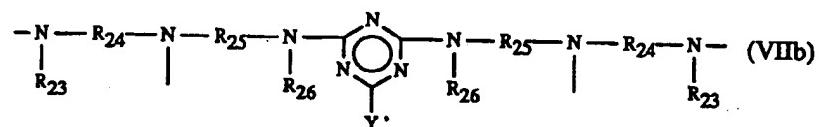
in which A_4 , A_6 , A_8 , A_9 and A_{10} which can be identical or different are as defined above for A_1 and A_2 , and, if A_8 and A_9 both are $-\text{O}$ -, A_{10} can also be a $-\text{CH}_2\text{O}$ - group, R_{11} , R_{12} , R_{13} and R_{18} which can be identical

or different are C_2 - C_6 alkylene, p is zero or 1, R_{14} , R_{15} , R_{16} , R_{17} and R_{18} which can be identical or different are as defined above for R_6 , A_7 is a direct bond or $-CH_2-$, q, r and s which can be identical or different are integers from 2 to 6 and R_{20} is hydrogen or C_1 - C_6 alkyl, and, if m is 4, Z is one of the groups of the formulae (VIIa)-(VIId)

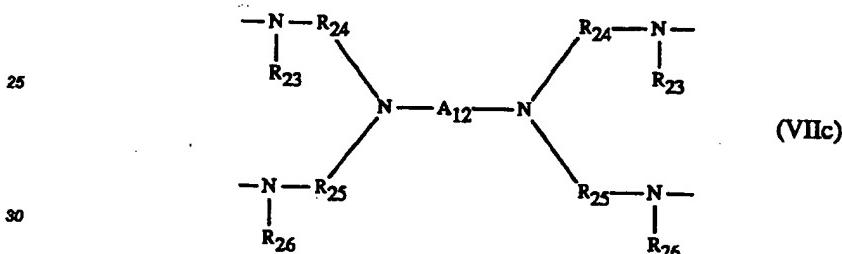
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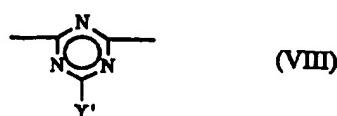
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In which A_{11} is as defined above for A_1 and A_2 , R_{21} , R_{22} , R_{24} and R_{26} which can be identical or different are C_2 - C_6 alkylene, t is zero or 1, R_{23} and R_{26} which can be identical or different are as defined above for R_6 , Y' is as defined for Y , A_{12} is 2-hydroxytrimethylene, $-CH_2CO-$, xylylene, aliphatic or aromatic diacyl having not more than 12 carbon atoms, a group $-COO(CH_2)_{4-6}OOC-$ or a group of the formula (VIII)

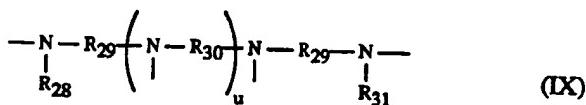
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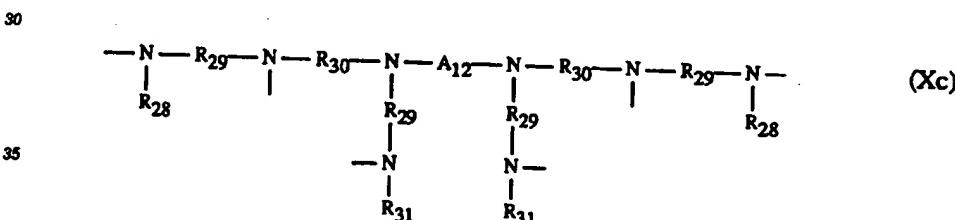
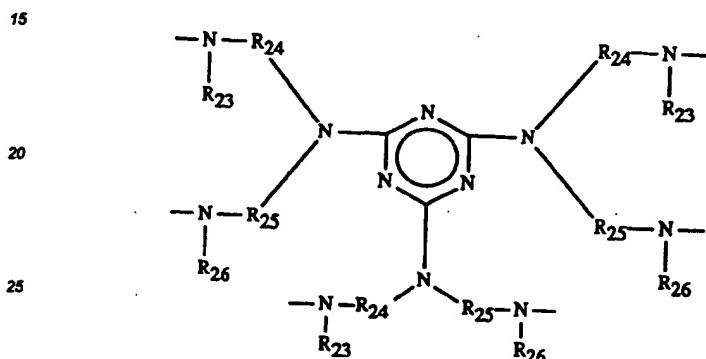
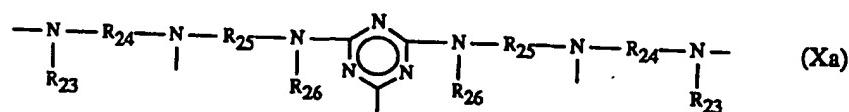
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where Y' is as defined above, and R_{27} is C_4 - C_{12} alkanetetrayl, and, if m is 5 or 6, Z is a group of the formula (IX)

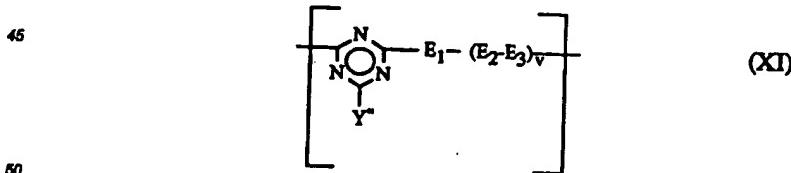
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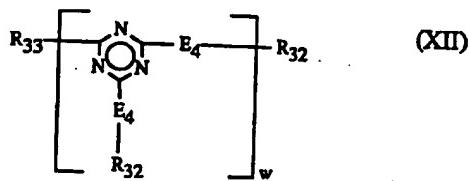
in which R₂₈ and R₃₁, which can be identical or different are as defined above for R₉, R₂₉ and R₃₀ which can be identical or different are C₂-C₆alkylene and u is 2 or 3, and, if m is 6, Z is also a group of the formulae (Xa)-(Xc)



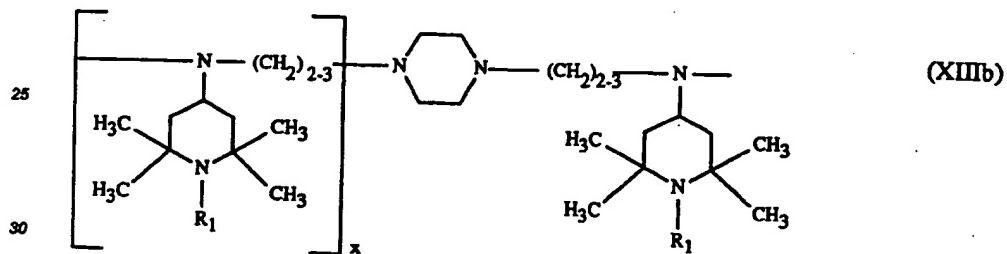
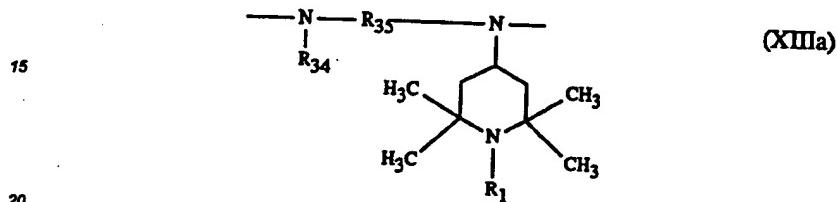
40 with R₂₃, R₂₄, R₂₅, R₂₆, R₂₈, R₂₉, R₃₀, R₃₁ and A₁₂ being as defined above;
b) oligomers having a molecular weight between 1,000 and 10,000 and containing recurring units of the formula (XI)



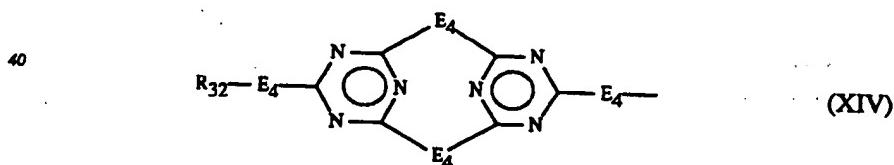
50 in which Y" is as defined above for Y, E₁ and E₃ which can be identical or different are groups of the formulae (Xa)-(Xc), E₂ is as defined above for A₁₂ and v is zero, 1, 2, 3 or 4, with the proviso that at least one group of the formula (III) must be present in each recurring unit of the formula (XI);
c) oligomers of the formula (XII)



10 in which R₃₂ is hydrogen, C₁-C₆alkyl, C₃-C₆alkenyl, C₇-C₉phenylalkyl, C₁-C₆acyl or (C₁-C₆alkoxy)-carbonyl,
E₄ is a group of the formula (XIIIa) or (XIIIb)



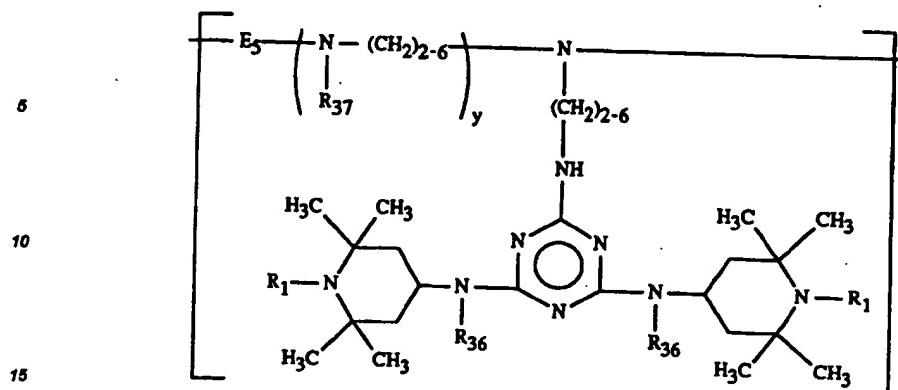
in which R₃₄ is as defined above for R₉, R₃₅ is C₂-C₁₂alkylene, cyclohexylene, cyclohexylenedimethylene,
35 methylenedicyclohexylene, xylylene or C₄-C₁₂alkylene interrupted by 1, 2 or 3 oxygen atoms or by a group
>N-CH₃, R₁ is as defined above and x is zero or 1, R₃₃ is OH, ONa, OX, C₁-C₆alkoxy, C₃-C₆alkenyloxy,
C₇-C₉phenylalkoxy, C₁-C₆acyloxy, a group R₃₂-E₄- or a group of the formula (XIV)



and w is a number from 1 to 20;
d) oligomers having a molecular weight between 1,000 and 10,000 and containing recurring units of the
formula (XV)

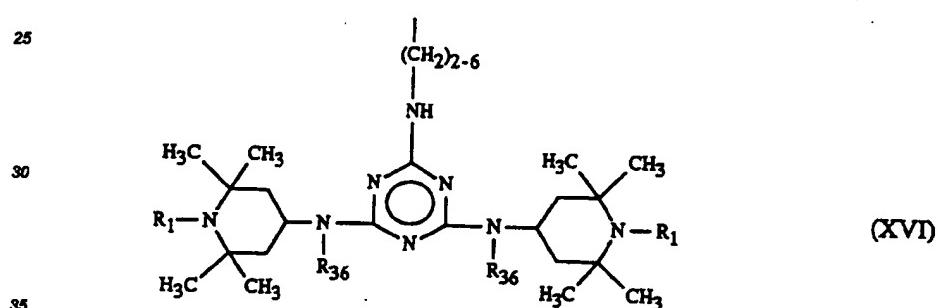
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(XV)

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in which R₁ is as defined above, R₃₆ is as defined above for R₂, R₃₇ is hydrogen, C₁-C₁₂alkyl, a group of the formula (III) or a group of the formula (XVI)

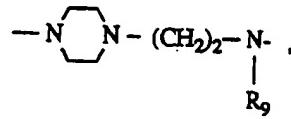


y is zero or 1 and E₅ is as defined above for E₂ or C₂-C₆alkylene.

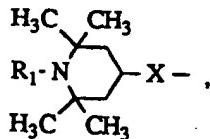
- 40
3. A stabiliser composition according to claim 1, wherein the compound (A) containing groups of the formula (I) is selected from the group comprising compounds of the formula II) in which R₁ is hydrogen, methyl, allyl, benzyl or acetyl, X is -O- or >N-R₂, R₂ is hydrogen, C₁-C₁₂alkyl, C₂-C₆alkyl substituted in the 2- or 3-position by C₁-C₄alkoxy, by dimethylamino, by diethylamino or by 4-morpholinyl, cyclohexyl, benzyl, tetrahydrofurfuryl or a group of formula (III) with R₃ being as defined above for R₁, Y is a group



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m is an integer from 2 to 6 and, if m is 2, Z is a group of the formula (Va) in which A₁ and A₂ are >N-R₆ with R₆ being hydrogen, C₁-C₁₂alkyl, cyclohexyl, benzyl or a group of the formula (III), R₇ is C₂-C₆alkylene, cyclohexylenedimethylene, methylenedicyclohexylene, xylylene or C₄-C₁₀alkylene interrupted by 1 or 2 oxygen atoms or by 1 or 2 >N-R₁₀ groups where R₁₀ is hydrogen, C₁-C₁₂alkyl, cyclohexyl, benzyl, a group of the formula (III), C₁-C₄acyl or (C₁-C₄alkoxy)-carbonyl, or Z is a group



and, if m is 3, Z is a group of the formula (Vla) in which A_4 and A_5 are as defined above for A_1 and A_2 , R_{11} and R_{12} which can be identical or different are $\text{C}_2\text{C}_6\text{alkylene}$ and p is zero, and, if m is 4, Z is a group of the formula (Vlla) or (Vllc) in which A_{11} is as defined above for A_1 and A_2 , R_{21} , R_{22} , R_{24} and R_{25} which can be identical or different are $\text{C}_2\text{C}_6\text{alkylene}$, t is zero, R_{23} and R_{26} are as defined above for R_9 and A_{12} is aliphatic or aromatic diacyl having not more than 10 carbon atoms or a group $-\text{COO}(\text{CH}_2)_{4-5}\text{OOC}-$, and, if m is 5 or 6, Z is a group of the formula (IX) in which R_{28} and R_{31} are as defined above for R_9 , R_{29} and R_{30} which can be identical or different are $\text{C}_2\text{C}_6\text{alkylene}$ and u is 2 or 3, and, if m is 6, Z is also a group of the formula (Xc) with R_{28} , R_{29} , R_{30} , R_{31} and A_{12} being as defined above; oligomers having a molecular weight between 1,000 and 5,000 and containing recurring units of the formula (XI) in which Y'' is one of the groups



25 R_4O - and



35 where R_1 and X are as defined above, and R_4 , R_6 and R_8 which can be identical or different are as defined above for R_2 , or

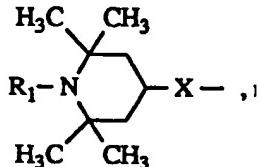


is 4-morpholinyl, E_1 and E_3 which can be identical or different are groups of the formulae (Va)-(Vc) where A_1 , A_2 and R_7 are as defined above, R_8 is hydrogen or methyl, A_9 is a direct bond and n is zero; E_2 is 2-hydroxytrimethylene, aliphatic or aromatic diacyl having not more than 10 carbon atoms, a group $-\text{COO}(\text{CH}_2)_{4-6}\text{OOC}-$ or a group of the formula (VIII) where Y' is as defined for Y'' and v is zero, 1 or 2, with the proviso that at least one group of the formula (III) must be present in each recurring unit of the formula (XI); oligomers of the formula (XII) in which R_{32} is hydrogen, $\text{C}_1\text{-C}_4\text{alkyl}$, $\text{C}_1\text{-C}_4\text{acyl}$ or $(\text{C}_1\text{-C}_4\text{alkoxy})\text{-carbonyl}$, E_4 is a group of the formula (XIIa) or (XIIb) in which R_{34} is as defined above for R_9 , R_{35} is $\text{C}_2\text{C}_6\text{alkylene}$, cyclohexylenedimethylene, methylenedicyclohexylene or $\text{C}_4\text{-C}_{10}\text{alkylene}$ interrupted by 1 or 2 oxygen atoms or by an $>\text{N---CH}_3$ group, R_1 is as defined above and x is zero or 1, R_{33} is OH, ONa, OK, $\text{C}_1\text{-C}_4\text{alkoxy}$, $\text{C}_1\text{-C}_4\text{acyloxy}$, a group $\text{R}_{32}\text{-E}_4$ or a group of the formula (XIV) and w is a number from 1 to 10; oligomers having a molecular weight between 1000 and 5000 and containing recurring units of the formula (XV) in which R_1 is as defined above, R_{36} is as defined above for R_2 , R_{37} is hydrogen, $\text{C}_1\text{-C}_{12}\text{alkyl}$, a group of the formula (III) or a group of the formula (XVI), y is 1 and E_5 is as defined above for E_2 or $\text{C}_2\text{C}_6\text{alkylene}$.

4. A stabiliser composition according to claim 1, wherein the compound (A) containing groups of the formula

(I) is selected from a) the group comprising the compounds of the formula (II) in which R₁ is hydrogen or methyl, X is >N-R₂, R₂ is C₁-C₆alkyl, 2,2,6,6-tetramethyl-4-piperidyl or 1,2,2,6,6-pentamethyl-4-piperidyl, Y is a group

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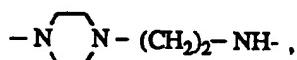


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m is 2, 3 or 4 and, if m is 2, Z is a group of the formula (Va) in which A₁ and A₂ are >N-R₉ with R₉ being hydrogen, C₁-C₄alkyl, 2,2,6,6-tetramethyl-4-piperidyl, or 1,2,2,6,6-pentamethyl-4-piperidyl, R₇ is C₂-C₆alkylene, cyclohexylenedimethylene, methylenedicyclohexylene, xylylene or C₄-C₁₀alkylene interrupted by 1 or 2 oxygen atoms or by an >N-R₁₀ group where R₁₀ is hydrogen, methyl, cyclohexyl, benzyl, C₁-C₄acyl or (C₁-C₄alkoxy)-carbonyl, or Z is a group

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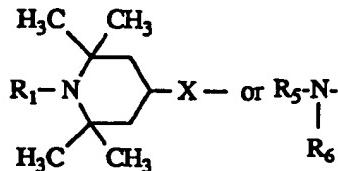


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and, if m is 3, Z is a group of the formula (Vla) in which A₄ and A₆ are as defined above for A₁ and A₂, R₁₁ and R₁₂ which can be identical or different are C₂-C₆alkylene and p is zero, and, if m is 4, Z is a group of the formula (VIIa) or (VIIc) in which A₁₁ is as defined above for A₁ and A₂, R₂₁, R₂₂, R₂₄ and R₂₅ which can be identical or different are C₂-C₆alkylene, t is zero, R₂₃ and R₂₆ are as defined above for R₉ and A₁₂ is aliphatic C₂-C₁₀diacyl or a group -COO(CH₂)₄₋₆OOC; b) oligomers having a molecular weight between 1,500 and 5,000 and containing recurring units of the formula (XI) in which Y" is one of the groups

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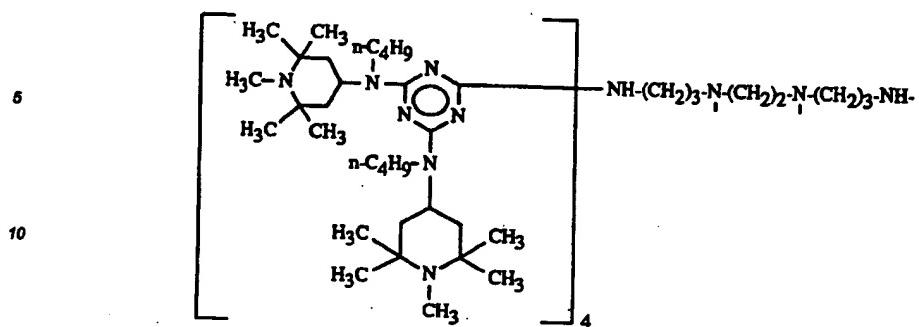
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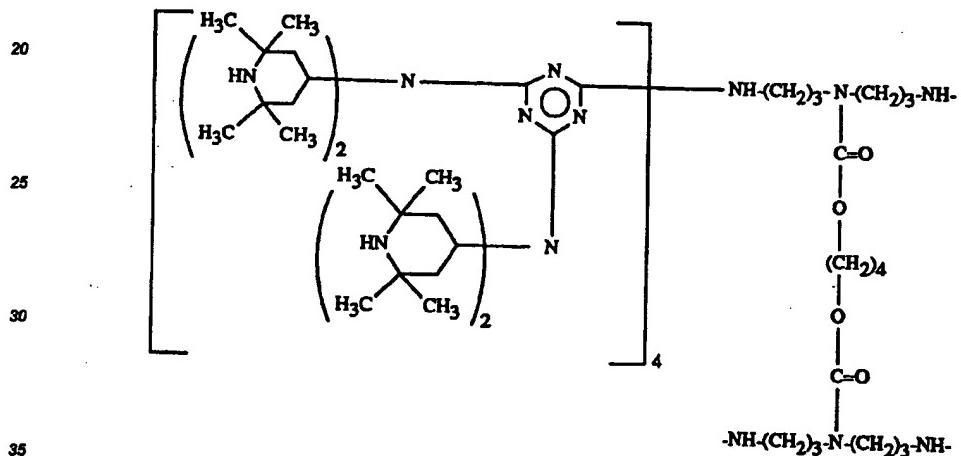
is 4-morpholinyl, E₁ is a group of the formula (Va) as defined above and v is zero, with the proviso that at least one group of the formula (III) must be present in each recurring unit of the formula (XI); oligomers of the formula (XII) in which R₃₂ is hydrogen, methyl, acetyl or (C₁-C₂alkoxy)-carbonyl, E₄ is a group of the formula (XIIIa) in which R₃₄ is 2,2,6,6-tetramethyl-4-piperidyl or 1,2,2,6,6-pentamethyl-4-piperidyl, R₃₅ is C₂-C₆alkylene or C₆-C₁₀alkylene interrupted by 2 oxygen atoms, R₁ is as defined above, R₃₃ is a group R₃₂-E₄ or a group of the formula (XIV) and w is a number from 1 to 5; c) oligomers having a molecular weight between 1,500 and 5,000 and containing recurring units of formula (XV) in which R₁ is as defined above, R₃₄ is as defined above for R₂, R₃₇ is hydrogen or a group of the formula (XVI), y is 1 and E₅ is C₂-C₄alkylene.

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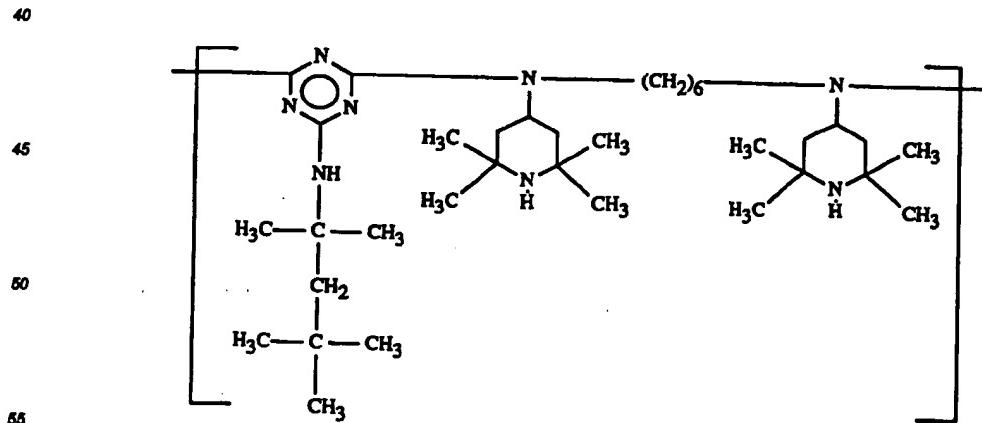
5. A stabiliser composition according to claim 1, wherein the compound (A) is that of the formula



6. A stabiliser composition according to claim 1, wherein the compound (A) is that of the formula

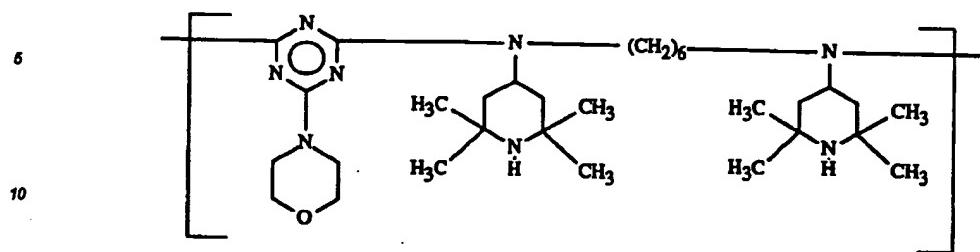


7. A stabiliser composition according to claim 1, wherein the compound (A) is an oligomer having a molecular weight of 1500 to 4000 containing recurring units of the formula

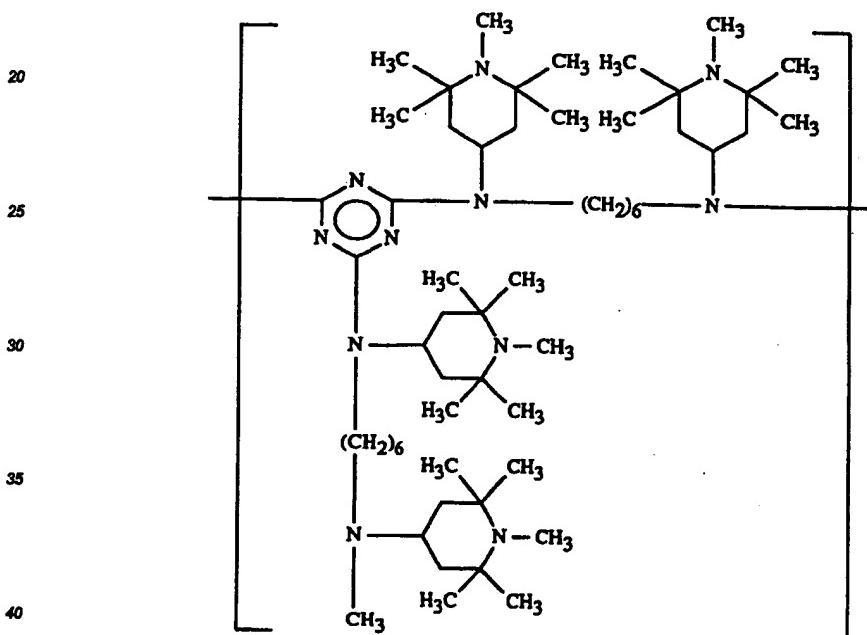


8. A stabiliser composition according to claim 1, wherein the compound (A) is an oligomer having a molecular

weight of 1500 to 4000 containing recurring units of the formula



9. - A stabiliser composition according to claim 1, wherein the compound (A) is an oligomer having a molecular weight of 1500 to 4000 containing recurring units of the formula

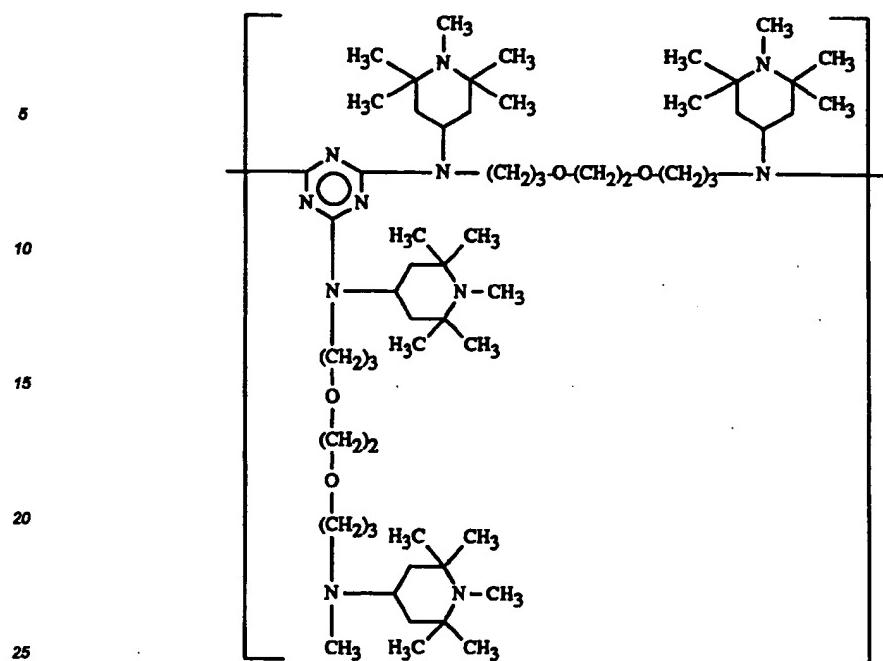


10. A stabiliser composition according to claim 1, wherein the compound (A) is an oligomer having a molecular weight of 1500 to 4000 containing recurring units of the formula

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11. A stabiliser composition according to claim 1 wherein the compound B is magnesium oxide or zinc oxide.

30 12. A stabiliser composition according to claim 1 wherein the weight ratio of A:B is from 1:0. 1 to 1:2.

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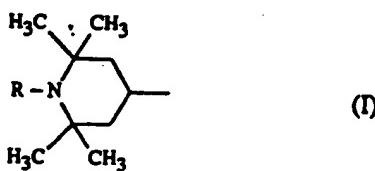
(88) Date of deferred publication of search report :
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(54) Stabiliser compositions for polypropylene, comprising triazine compounds containing piperidine groups, and metal compounds.

(57) The present invention relates to a stabiliser composition for polypropylene, comprising :

A) one or more triazine compounds containing groups of the formula (I) in which R is hydrogen, C₁-C₄alkyl, O-, OH, C₁-C₈alkoxy, C₅-C₈cycloalkoxy, C₃-C₆alkenyl, C₇-C₉phenylalkyl or C₁-C₈acyl, and

B) one or more oxides and hydroxides of Mg, Ca, Ba, Zn, Al and Sn, preferably Mg and Zn.



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**European Patent
Office**

EUROPEAN SEARCH REPORT

Application Number

EP 91 81 0576

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL.5)
A	EP-A-0 290 388 (CIBA-GEIGY AG) * claim 1 *	1	C08K13/02 C08L23/12
A	GB-A-2 132 621 (EXXON RES. ENG. COMP.) * page 3; claim 1 *	1	

TECHNICAL FIELDS SEARCHED (Int. CL.5)			
C08K C08L			
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	02 DECEMBER 1992	Dieter Schüller	
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone	T : theory or principle underlying the invention		
Y : particularly relevant if combined with another document of the same category	E : earlier patent document, but published on, or after the filing date		
A : technological background	D : document cited in the application		
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P : intermediate document	& : member of the same patent family, corresponding document		